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CHIP DESORPTION AND PORE STRUCTURE EFFECTS IN METHANE RELEASE FROM COAL

Final Report: Volume 1

By
Frank L. Williams

January 1983

Work Performed Under Contract No. AC21-81MC16015

For
Morgantown Energy Technology Center
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By
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Albuquerque, New Mexico

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Volume I

Final Report

on

CHIP DESORPTION AND PORE STRUCTURE EFFECTS IN METHANE RELEASE FROM COAL

by

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EXECUTIVE SUMMARY

Engineering aspects of methane release from coal have been studied in order to define the mechanisms which are operative during the delineation of methane by the chip desorption technique and during gas generation prior to crack flow into a production well. In addition, characterization of the surface area and pore structure of the test coal (Fruitland coal, San Juan Basin) revealed a basic understanding of methane storage mechanisms and resource delineation strategies. The results of this work have been written as six papers to be published in journals and/or proceedings of conferences, a Master of Science thesis, and a Ph.D. dissertation. This report consists of a summary of the task required accomplishments and copies of the other written material as appendices.

As a result of our work, we have been able to conclude that:

- the chip desorption technique and associated lost-gas correction factors are valid coalbed methane delineation techniques,
- basin wide coalbed methane delineation is very site specific and seems to defy normal trend expectations. Therefore, multiple site testing is required for reasonable resource definition,
- coalbed methane content appears to be geologically influenced much more strongly than limited by equilibrium adsorption capacity,
- diffustion of methane through coal should be described by a two parameter model which properly gives gas evolution rates over both short and long times. This model is directly applicable as a source term in production models,

- surface properties of coal as measured at low pressures do not seem to relate to the high pressure measurements of the methane adsorption capacity.

As a result of this study, and the considerable field work associated with it, the DOE has promulgated a delineation technique and stimulated commercial activity in the San Juan Basin of northern New Mexico and southern Colorado. Recommendations for further work call for studies related to the completion and production strategies for particular basins.

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INTRODUCTION

This project was conceived as essentially a laboratory-based, experimental study of basic engineering fundamentals required to complete development of the chip desorption technique, define the basic understanding of the storage, desorption, and diffusion of methane within the coal structure, and give a better source term for production models. Samples of coal, which were obtained from drilling operations within the San Juan Basin of New Mexico, were subjected to a number of laboratory tests to determine the physical properties and methane flow characteristics of the coal chips. This report presents those results in light of their importance to methane recovery from coalbeds.

In the main body of this report, the results of the study are presented, by task, as they were defined in the modified proposal. Those results, and appropriate discussion, are given in the following task headings:

- Field Data Analysis
- Verification of Lost-Gas Correction Model
- High Pressure Adsorption Isotherms
- Physical Structure Properties
- Diffusion of Methane in Coal

PURPOSE AND OBJECTIVES

The purpose of this project was to allow development of a technique to rapidly and inexpensively determine the methane content of coalbeds. Specific objectives were defined as project tasks. The objectives were to consider a proper basis for resource delineation, to verify the model used to calculate a lost-gas correction for the technique being developed, to study the relationship between equilibrium adsorption and field content, to determine the physical structure of the test (Fruitland) coal and to measure diffusion properties of the coal in order to model gas evolution source terms.

PROJECT RESULTS AND DISCUSSION

The results of this project are so extensive and broadly applied to various phenomena that are important to delineation of coalbed methane, we have found it necessary to organize the results along the lines of the originally defined tasks. In order to avoid unnecessary repetition of the results, discussion of each type of result is given along with a presentation of representative data. The bulk of the data and mathematical analyses are preserved for reference in the appendices.

A major result of this work, that transcends the individual task accomplishments, is the extremely high visibility and acceptance of this work. This work has been reported at national meetings of the Society of Petroleum Engineers and the Rocky Mountain Fuel Society. This work is extensively published in the open literature where it is readily available for use in private industry. This work has led to the use of the technique by at least four gas exploration companies, three engineering consulting/service firms that help companies delineate their coalbed methane potential, and one university. Regardless of any problem with specific details of the project, it is evident that the purpose has been achieved and that DOE has facilitated implementation of a useful technique. In addition, field projects are ongoing in order to convert this resource, coalbed methane, into production reality.

Another overall result of this project is the training of researchers interested in production of energy from coal. A research group has been established at the University of New Mexico directly as a result of this project. Students graduating from the UNM group are now establishing coal research at Montana State University. Perhaps those results will have longer range effects toward the development of coalbed methane.

Field Data Analysis

Introduction

Prior to this project we had proposed and implemented a technique for delineating the methane content of coalbeds as a part of ongoing drilling operations. The technique is especially rapid and inexpensive. However, more work was required to validate the technique. First, let us review the technique.

Based on Bureau of Mines work by Kissel, et al., delineation of coalbed methane in the United States has been "directly" measured by desorbing methane from core samples of coal. Archer, et al., Ricke, and Termain have recently reported their results from core based sampling in the Illinois, Arkoma, and Raton basins, respectively. In fact, Wise and Rightmire and Schrider and Wise have described DOE plans for delineation of coalbed methane throughout major coal basins in the United States. Because of the expense of coring and the long times required for determining the gas content of the core samples, the delineation strategies have been restricted to a relatively few samples from any one basin where cooperative agreements between DOE and operators could be established. We have described a "direct" measurement technique, based on collection of drill cuttings, that is inexpensive, quick, and reduces the complexity of cooperative agreements. With those advantages, many more samples can be obtained in a basin and the sample locations are much more flexible.

Even in the early reports of "direct" measurement of coalbed methane, the possibility of determining the methane content of coal from drilling fines was recognized. We have modified the concepts of Bertard, et al. to properly account for gas lost from the cuttings as they are carried from the coal seam to the surface. That modification has allowed us to successfully sample coals as deep as 1000 m as a part of ongoing drilling operations.

Another advantage of measuring methane desorption from small drill cuttings (chips) is that residual gas determinations, like the decline curve calculations of Chase, are not required. Large pieces of coal, such as obtained by coring, desorb methane very slowly and therefore require some method of determining the amount of gas remaining in the coal after the desorption rate can no longer be accurately followed. That gas remaining in cores has been called residual gas and it can amount to a substantial fraction of the total gas content. Physical methods based on grinding the coal have been used to determine residual gas content. However, those procedures could be questioned because of the possibilities of making gas by grinding the coal and of allowing gas to escape from completely trapped volumes. Chase's decline curve calculations seem more likely to lead to realizable methane concentrations for cores. Desorption from small coal pieces is somewhat simpler. Airey's experimental measurements of desorption from recharged particles of coal and our field experience has shown that negligible desorption from chips occurs after about one week. Furthermore, that rate is less than the rate Chase used to define residual gas. Therefore, no extra determination is required.

The determination of the methane content of coal by use of the chip desorption technique is seen as a three-part process. First, the cuttings (coal chips) are collected from recirculating drilling fluids as a coalbed is penetrated in a conventional drilling operation. Then the chips are sealed in a canister so that the amount of gas evolving from the chips can be measured. Finally, the data are analyzed to adjust the gas content for lost gas and to correct the gas content for extraneous shale or water that may have been collected along with the coal. Each of these parts is described in detail in Appendix I.

This Work

The mass basis for reporting the methane content needed to be clarified. Obviously, the data could be reported as volume of gas at STP per unit mass of solid sample as collected. The mass of wet coal and other material in the container, exclusive of any liquids that can be drained off, can be readily and unambiguously determined. However, a problem arises when one tries to relate that mass to the geologists' basis for coal in place.

The sample is normally made up of coal, shale-like material that is normally considered part of the coal seam and that is included in the estimate of "in-place" coal, shale and sandstone stringers in the coal, and extraneous material that came from other open hole regions of the well drilling operation. Depending upon the drilling technique and the geology, various degrees of correction need to be made.

Throughout the San Juan basin, the Fruitland coals are thick and essentially free of stringers. The geologists' estimate of "in-place" coal and the drilled cuttings correspond to the same basis. Therefore, no need for correcting the mass basis is evident.

However, if extraneous material falls into the cuttings as they circulate up to be sampled, or if a seam is replete with stringers, then a correction is in order. While density separation of coal from rock is feasible, the technique changes the nature of the coal. We proposed a technique based on determining the ash content of the coal and of the gross sample. The technique also provides a way to relate the content to the adsorptive capacity of the organic coal alone.

To make the correction, each field sample was divided into two parts. Then, for one part, the coal was separated from shale

by visual inspection. For convenience, the coal which was separated from shale is named the separated sample and the other part of the original field sample is named the gross sample.

The ash content of the two different sets of samples, the moisture content of the gross samples, and the moisture content of the shales are determined by experiments. Utilizing these values, relatively simple equations have been derived to correct the raw gas contents obtained from the field. Those equations were derived based on the simple stoichiometric relationships for ash, moisture, and shale in the two different sets of samples. First, using the concept that ash fraction for the separated sample (coal only) is the same as that of the gross sample when the shale and sand portion in the gross sample is excluded, the shale content on a dry basis is expressed in terms of the ash contents of the gross and separated sample by the following equation:

$$DS = \frac{AG - AS}{1 - AS}, \qquad (1)$$

where DS = shale content of the gross sample based on dry state (weight fraction),

AG = ash content of the gross sample (weight fraction),

AS = ash content of the separated sample (weight fraction).

Then, the shale content based on dry state has to be converted to the value based on wet state. Because the amount of moisture held on the shale and sand is different from that on the coal, the moisture content of the shale and sand and those of the gross sample are determined by experiment. Considering this fact, the shale content based on wet state is expressed by Equation 2:

$$WS = \frac{DS + DS \times \frac{MS}{1 - MS}}{1 + \frac{M}{1 - M}} \qquad (2)$$

where WS = shale content of the gross sample based on wet state,

DS = the shale content of the gross sample based on dry state,

MS = moisture content of the shale,

M = moisture content of the gross sample.

Therefore, the gas content corrected for shale and sandstone on a wet basis can be calculated by using Equation 3:

$$CG = \frac{RG}{1 - WS}, \qquad (3)$$

where CG = gas content corrected for shale and sandstone,

RG = raw gas content from the field,

WS = shale content of the gross sample based on wet state (wt fraction).

The ash and moisture contents of each group were determined by following the ASTM standard procedures. All the samples used in the experiments were ground to pass 60 mesh.

The experimental procedure for moisture determination is:

1) Heat the empty crucible under the conditions at which the sample is to be dried, place the cover on the crucible, then cool it over H_2SO_4 for 30 minutes, and weigh.

2) Dip out with a spoon from the sample container approximately 1 g of trhe sample. Put this quickly into the crucible, close, and weigh at once.

3) After removing the cover, quickly place the bowl in a preheated oven (at 104 - 110°C).

4) Close the oven at once and heat for 1 hour.

5) Open the oven, cover the bowl quickly, then cool it in a desiccator over H_2SO_4 for 30 minutes, and weigh.

The experimental procedure for ash determination:

1) Place the crucible containing the dried coal sample from the moisture determination in a cold furnace and heat

gradually so that the temperature reaches 500°C in 1 hour, and increase the temperature up to 750°C, then keep it for 2 hours. By this method pyritic sulfur will be oxidized and expelled before the calcite is decomposed.

2) Open the oven, cover the bowl, cool it in a desiccator over H_2SO_4 for 30 minutes, and weigh.

All heating procedures were conducted in air in a Precision Theco Oven.

Ash, moisture, and shale content of the twelve coal samples where extraneous material was expected, were determined and their numerical values are shown in Table 1. Ash content of the separated coals ranged from 12.9 to 44 percent. Sample No. 11 has an unexpectedly high ash content. Most of the samples have high ash contents of approximately 20 percent. However, it is generally known that western United States coal has high ash contents. The gas contents obtained by chip desorption technique are corrected using Equations 1, 2, and 3. The uncorrected gas content and corrected gas conent are shown in Table 2. The corrections for shales and extraneous materials caused gas content to increase by approximately 15 to 120 percent. The highest gas content among the corrected data is 8.34 cc/g which is equivalent to 267 cubic feet per ton.

While these results indicate a wide variation in the ash content of the coal itself, a wide variation in the amount of extraneous material collected, and a considerable correction needed to be made, it is important to realize that the samples were those that we knew needed the correction. In most cases the sampling was much more straightforward and all of the sample was "coal."

In addition to completing the objectives of this task as proposed, we looked at the field data from across the basin to determine what trends might exist. We were unable to find and

Table 1

Ash, Moisture, and Shale Content of the Coals

	Ash %		Moisture %		Shale %	
Sample	Separated	Gross	Shale	Total	Dry	Wet
1	12.90	37.14	1.5	25	16.7	12.7
2	19.54	34.54	1.5	25	16.6	12.6
3	18.35	40.39	3.8	28.7	27.1	20.1
4	24.85	49.66	3.3	31.3	33.0	23.4
5	17.63	53.62	2.4	16.7	47.3	40.4
6	23.22	66.24	1.9	21.1	56.0	45.0
7	25.97	51.93	2.2	26.7	35.0	26.2
8	19.33	70.60	2.0	16.9	63.5	53.8
9	35.23	64.52	2.7	22.3	45.2	36.1
10	35.23	52.68	2.7	22.0	26.9	21.6
11	44.04	74.42	5.6	16.2	43.5	38.6

Table 2

Comparisons of Uncorrected and Corrected Gas Content

Sample No.	Gas Content (cc/g) Uncorrected	Corrected	% Increase
1	1.98	2.27	14.6
2	1.47	1.69	14.9
3	6.67	8.34	25.0
4	3.62	4.73	30.6
5	2.90	4.87	67.9
6	1.46	2.66	82.2
7	3.23	4.38	35.6
8	1.85	4.01	116.7
9	2.25	3.52	56.4
10	1.65	2.10	27.3
11	2.48	4.04	62.9

correlate gas content with depth or location within the basin. The full results were presented and published as part of the SPE/DOE Symposium on Unconventional Gas Recovery which was held in Pittsburgh on May 17 and 18, 1982. A copy of that paper is included in this report as Appendix 2.

Verification of Lost-Gas Correction Model

As presented in the last section, the chip desorption technique for determining the methane content of coalbeds had been proposed before inception of this contract. However, detailed analysis of the lost-gas correction scheme had not been completed. That analysis has now been completed and has been submitted for publication in Fuel (Appendix 4).

Introduction

In order to estimate the quantity of gas lost during sample recovery, a model for the desorption process is required. The release of methane from small coal particles is considered as a two-state process. Desorption of the methane from the pore internal surfaces is followed by diffusion through the pores. Since methane is physicaloy adsorbed on coal, the time required for desorption is negligible as compared to the diffusion step. Thus, predicting the lost gas reduces to finding a realistic diffusion model and a means of determining the required model parameters. Historically, the "unipore" diffusion model has been applied to coal. This model, also known as the "parallel pore" model, was developed by Wheeler for use with porous catalyst pellets exhibiting well-defined pore structures. This model assumes that the porous solid is interspersed with non-connecting cylindrical pores of one radius. Previous investigators who used the unipore model for coal are in some disagreement concerning the applicability of this model for describing diffusion rates for the entire timescale of desorption.

In order to assess the validity of the unipore model for coal, we have conducted an experimental investigation of methane desorption from coal drill cuttings. The unipore model was found to be adequate for describing the first 50 percent of desorption

and has been incorporated into a technique for predicting the quantity of gas lost during sample recovery. In addition, a diffusion model is presented which more realistically describes the physical structure of coal and accurately describes diffusion rates for both small and large times. This predictive capability is especially important to overall gas production models for a well.

Results/Unipore Model

A total of six desorption runs were conducted. Effective diffusivities are calculated by matching a first-order, least-squares fit of the data for the first 600 seconds of desorption. The calculated values of D_e are presented in Table 3. Immediately apparent is the relatively narrow range of D_e considering that all samples are from widely different parts of the same formation. Of more importance to this work is to determine the extent to which the diffusivity, which is calculated from data taken at short times only, can correlate experimental desorption data over the entire timescale of the desorption. The fraction of gas desorbed for all times may be calculated from:

$$\frac{V}{V_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty} \frac{1}{n^2} \exp^{(-D_e n^2 \pi^2 t)}$$

For all 6 runs, experimentl data and Equation 4 agreed well for $V/V_\infty < .5$, but significant deviation between the unipore model and experimental values occurred at larger V/V_∞ values. This deviation is illustrated for 2 samples in Figure 1. These two samples are presented since they represent extremes in the magnitude of D_e. Although the unipore model is inadequate for all time, the results of this work indicate that it may be used to predict methane lost during the recovery of drill cuttings if sample times are on the order of 30 minutes.

Table 3. Calculated diffusion coefficients for the unipore and bidisperse pore models

Sample #	Depth (m)	Unipore $D_e(sec^{-1})$	Bidisperse Pore $D_i(sec^{-1})$	$D_a(sec^{-1})$	$\Delta(sec^{-1})$
Dome #2	428	7.93×10^{-6}	1.80×10^{-6}	1.21×10^{-5}	2.88×10^{-6}
Susco Biddoni #1	367	2.26×10^{-5}	2.78×10^{-6}	3.71×10^{-5}	2.89×10^{-6}
SX #1-18	349	8.17×10^{-6}	2.22×10^{-6}	2.33×10^{-5}	6.76×10^{-6}
B/N 45A	917	1.43×10^{-5}	1.79×10^{-6}	1.63×10^{-5}	1.43×10^{-6}
B/N 31A	915	1.94×10^{-5}	5.28×10^{-6}	5.18×10^{-5}	8.18×10^{-6}
B/N 24R	954	1.74×10^{-5}	1.80×10^{-6}	2.57×10^{-5}	1.71×10^{-6}

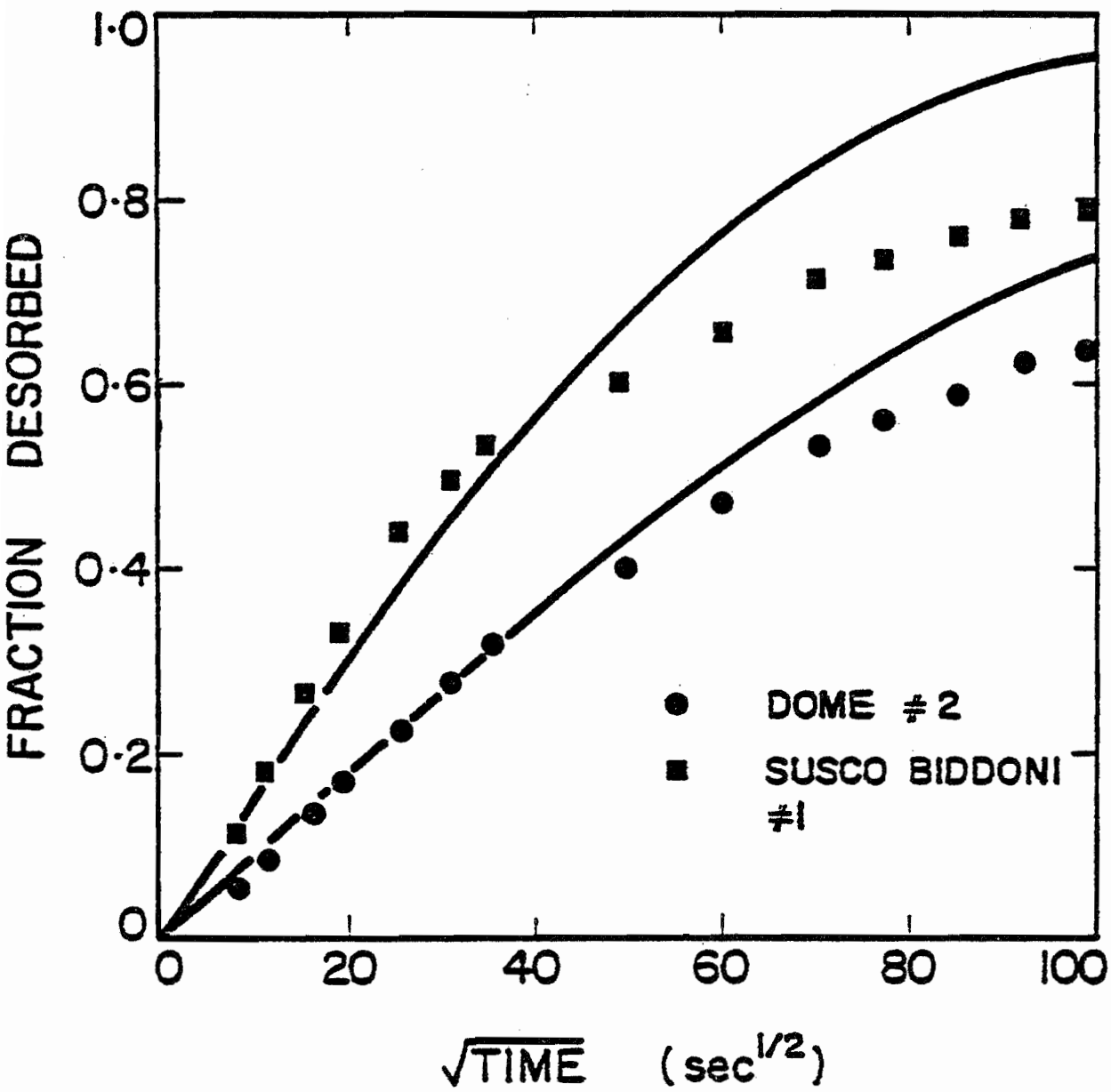

Figure 1 Comparison of experimental desorption and unipore model.

In conclusion, we were able to show that methane desorption from recharged coal chips does follow a single parameter diffusion model for the first half of gas evolution. With that bound for the applicable correction factors, the scheme was shown to be valid. Further verification was made by direct comparison of the chip technique to the direct technique at proprietary sites. The two techniques compared within 10 percent at gas contents of 500 SCF/ton.

These studies also showed that a single parameter model was not sufficient to describe desorption during the last half of gas evolution. For those times, a two-parameter model has been developed so that the desorption rate can be described over the full-time scale of gas evolution. That result is especially important for modeling methane production at the well head.

Additional Results

This more complete description of the gas evolution from coal has also been applied to the lost gas correction scheme used with the direct method. Most of the delineation studies conducted in the U.S. use the "direct" method developed by the U.S. Bureau of Mines. Despite the widespread use of this method, questions still exist about its accuracy. In particular, as sampling is conducted at ever-increasing depths, the reliability of the technique for determining the quantity of gas lost during sample retrieval becomes questionable. The bidisperse pore model has been used to quantify errors associated with this technique and to present a modification which incorporates the actual pressure history of the core.

Core retrieval and sampling is a two-step process. The first step is the time from seam penetration to sample surfacing. During this period of time, T_D, the surface pressure of the core decreases linearly with time. The second step involves

removal of the sample from the core barrel, various measurements and placement into the sample container. During this second period of time, T_S, the surface pressure is constant. Obviously, the quantity of lost gas will be a function of both the total time ($T_D + T_S$) during which gas is lost, and the fraction of time at the surface [$T_S/(T_D + T_S)$]. The second variable is neglected in the present Bureau of Mines' method. Depending upon the seam depth, sampling procedure and core retrieval problems, this second variable may range between .1 and .8.

The exact quantity of gas lost during the sampling procedure may be determined by using the fact that the unipore diffusion model is valid for coal for $V/V_\infty < .5$ where V_∞ is the total volume of "desorbed " and "lost" gas. The solution of this model with the boundary conditions described in the previous paragraph has been obtained previously by Smith and Williams. This solution may be used to predict the quantity of gas desorbed as a function of time. Plotted in Figure 2 are both the exact solution and the Bureau of Mines' approximation for the case when $T_S/(T_D + T_S) = 0$. For clarity, the quantity of gas desorbed, V/V_∞, is plotted in dimensionless time where τ is the product of effective diffusivity and time. Note that for this case, the exact quantity of lost gas, V_c, is approximately 10 percent less than that predicted with the Bureau of Mines' method, V_b. This result is independent of effective diffusivity and T_D. This suggests that by determining the ratio of V_c/V_b as a function of the surface time ratio, $T_S/(T_S + T_D)$, a simple multiplicative correction factor may be defined. Presented in Figure 3 is this correction factor (V_c/V_b) as a function of the surface time ratio. At large surface time ratios, the Bureau of Mines' method significantly underpredicts the quantity of lost gas.

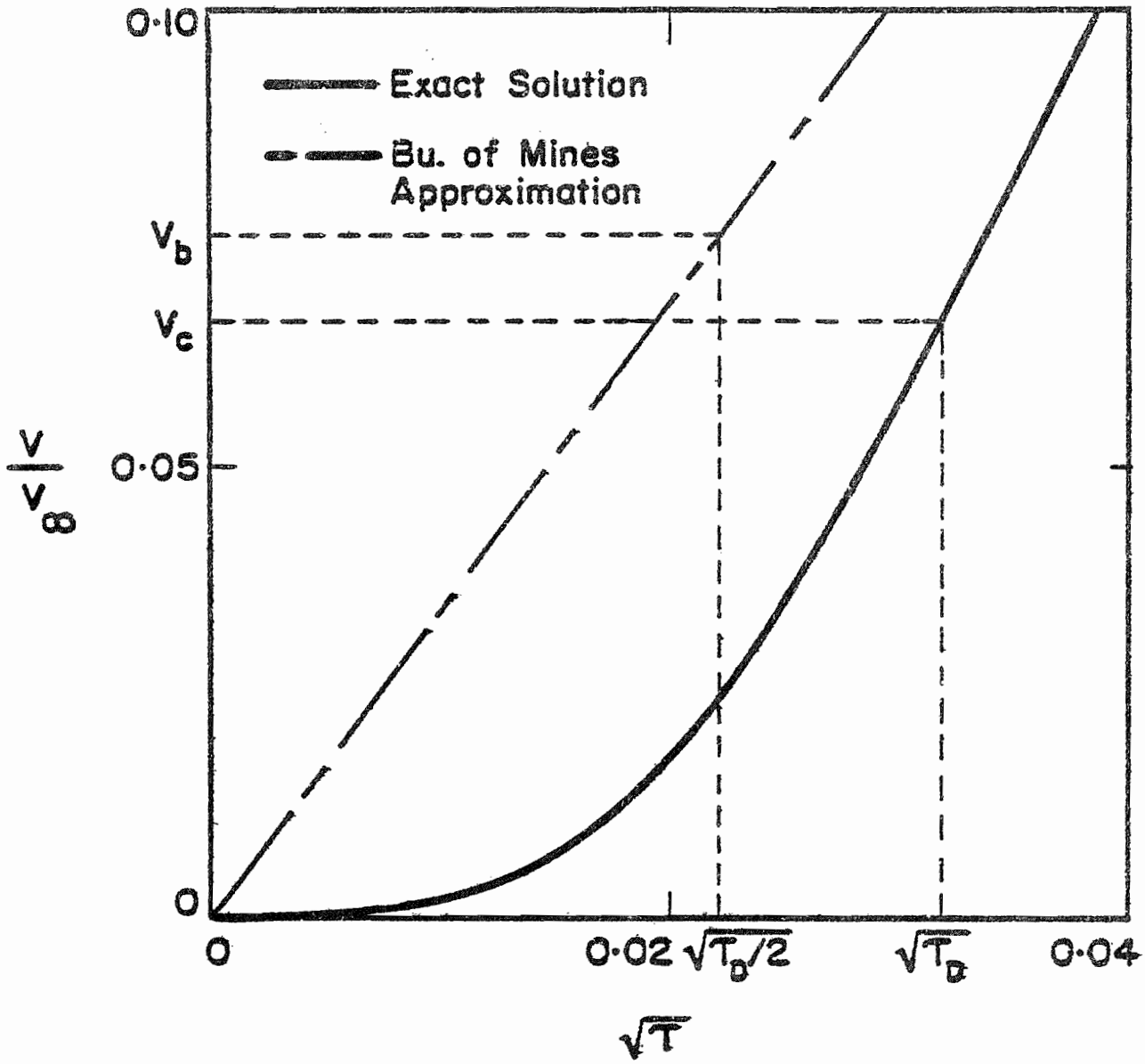

Figure 2 Exact and approximate lost gas determination techniques.

The application of this modification is straightforward. After one determines the lost gas by the present "direct" method, the surface time ratio is calculated. Both T_S and T_D are easily observed in the field. With this ratio known, the correction factor may be determined from Figure 3. Multiplying this correction factor by the lost gas calculated with the "direct" method results in the determination of the correct amount of gas lost during the core retrieval and sampling process.

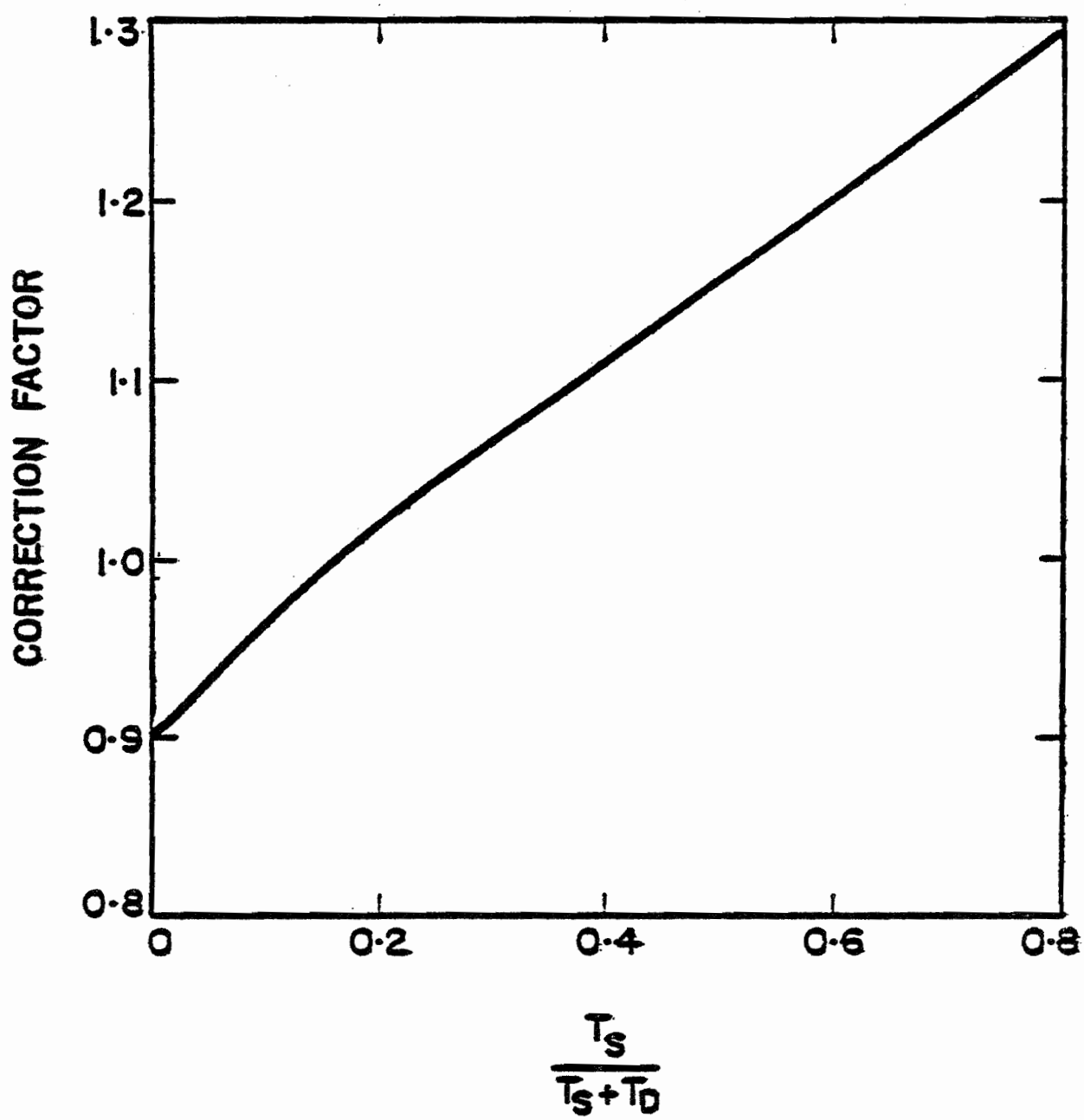

Figure 3 Volume correction factors to the lost gas calculated by the Direct method.

High Pressure Adsorption Isotherms

The intrinsic capacity for these Fruitland, subbituminous coals to adsorb methane has been measured. The coal was found to have a much higher capacity than is found in the field. Basically, coalbed methane content is determined by local geological features rather than equilibrium thermodynamics.

Methane adsorption on dry coal

All coal samples used in this study exhibited a smooth adsorption isotherm that fit the classical Langmuir form. As an example of the adsorption data, Figure 4 shows the volume of methane adsorbed on one of the coal samples as a function of the equilibrium pressure of methane. In order to abstract the monolayer capacity for methane adsorption and the adsorption constants associated with the Langmuir isotherm, the data are replotted in a linearized form of the Langmuir isotherm as shown in Figure 5. The data do fall on a good straight line, thereby confirming the validity of the model over this range of pressures. The constants determined from such linearized plots for each of the coal samples is summarized in Table 4.

The high pressure data are compared with the low pressure data (Appendix 7) in Figure 6. All of the data systematically lie to the right of the line drawn with slope of one. The low pressure CO_2 areas group along a line that underpredicts the apparent high pressure surface area by about 40 percent. The low pressure methane adsorption data also group along a line, but the surface areas are underpredicted by about 60 percent. These results are under investigation.

Methane adsorption on wet coal

The reduction in methane adsorption with increasing water content can be readily seen in Figure 7. Surprisingly, the data are still described by a Langmuir isotherm as evidenced in

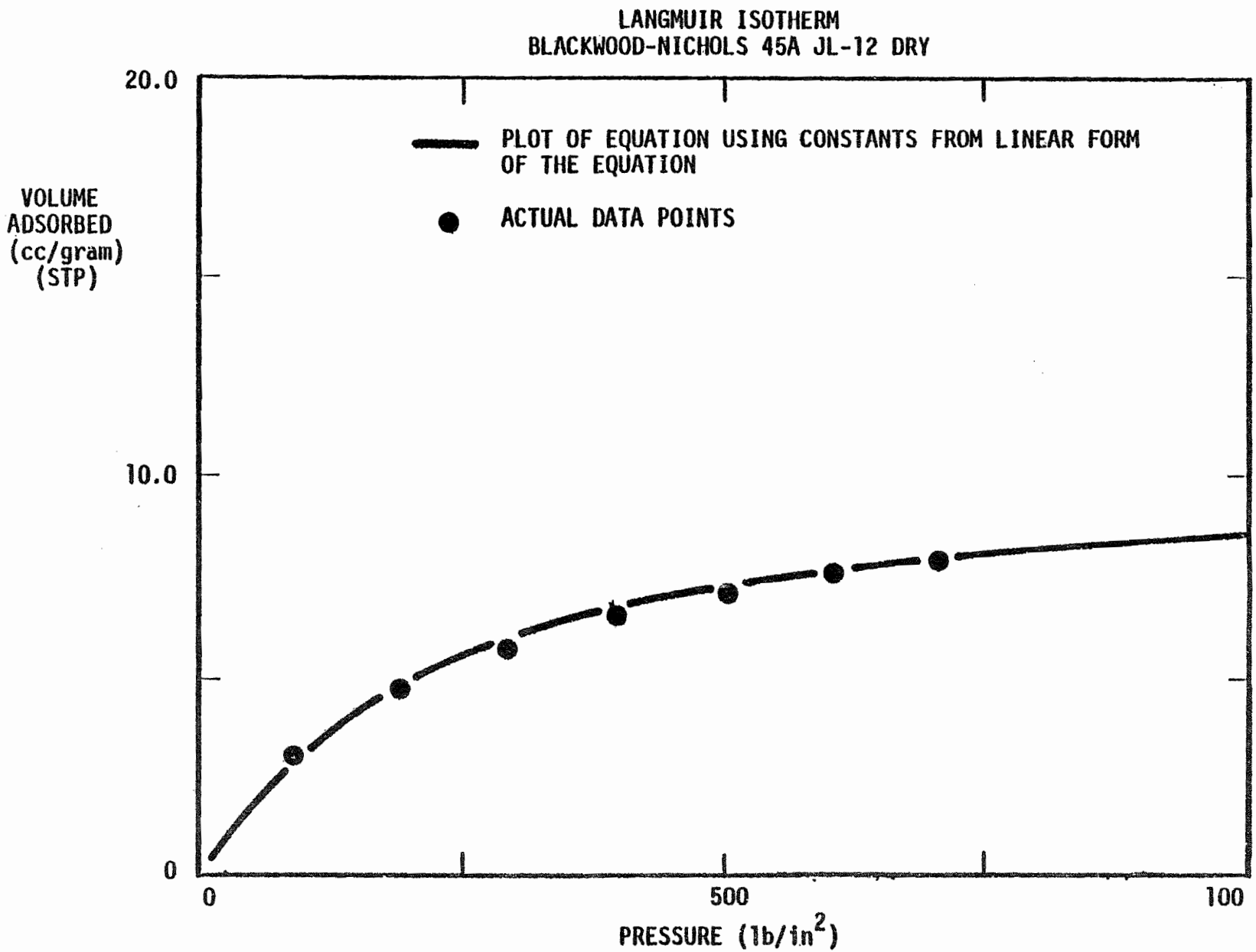

Figure 4 Methane adsorption on dry coal.

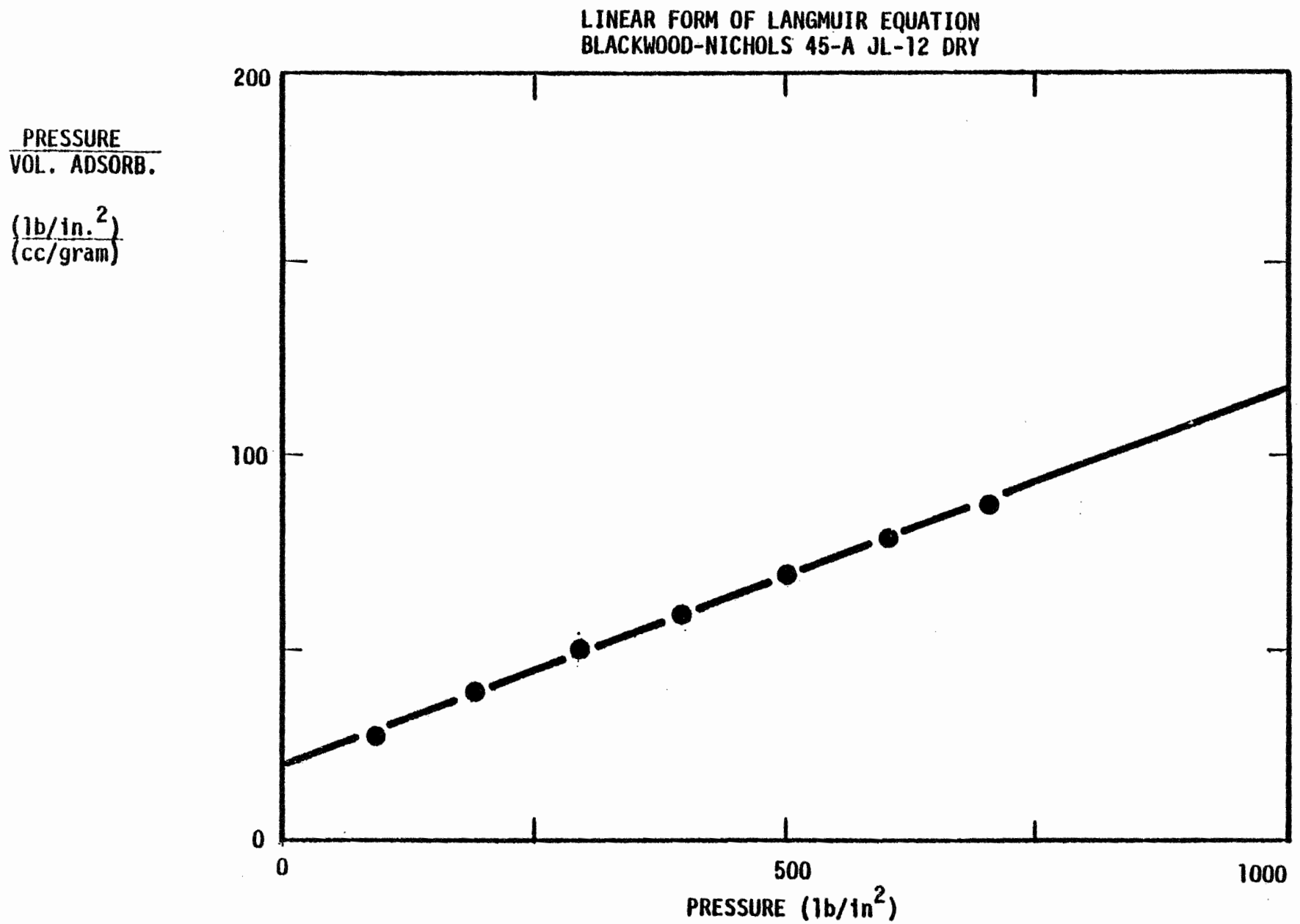

Figure 5 Linearized Langmuir adsorption isotherm for methane on dry coal.

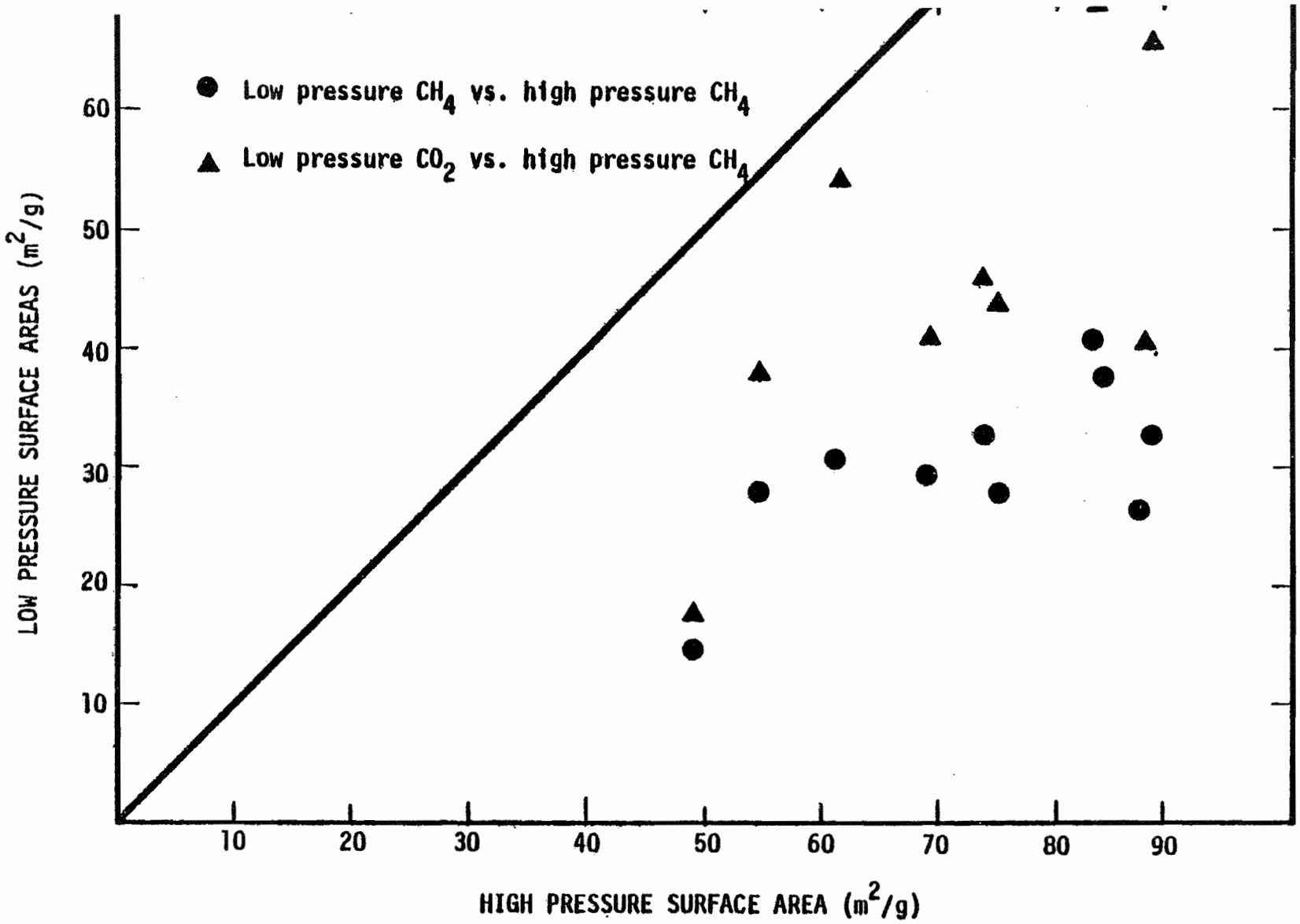

Figure 6 Attempted correlation of high pressure and low pressure surface area measurements.

Table 4

Dry Coal Monolayer Capacities (Langmuir) and Langmuir Constants

Sample No.	Description	Monolayer Capacity, Vm (cc/gram, gross)	Adsorption Constant, K	Monolayer Capacity, Vm (cc/g coal)
1	SX-Susco Biddoni	15.48	0.0034	20.4
2	SX-Federal 1-18	14.89	0.0032	18.3
3	Dome #2	14.11	0.0033	19.3
4	Dome #3 JL-12			
5	B/N 24R JL-18	9.78	0.0040	17.4
6	B/N 24R JL-18	7.07	0.0036	16.0
7	B/N 31A JL-18	7.41	0.0033	12.7
8	B/N 31A JL-18	7.41	0.0033	20.3
9	B/N 45A JL-9	9.35	0.0042	17.1
10	B/N 45A JL-12	10.40	0.0045	14.2
11	NW #51	5.21	0.0035	11.4
12	Western Coal	20.17	0.0046	
13	Sunbelt Coal	24.16	0.0030	
14	Pittsburgh Seam Coal	16.86	0.0048	
15	Madrid Antra-cite	26.59	0.01005	

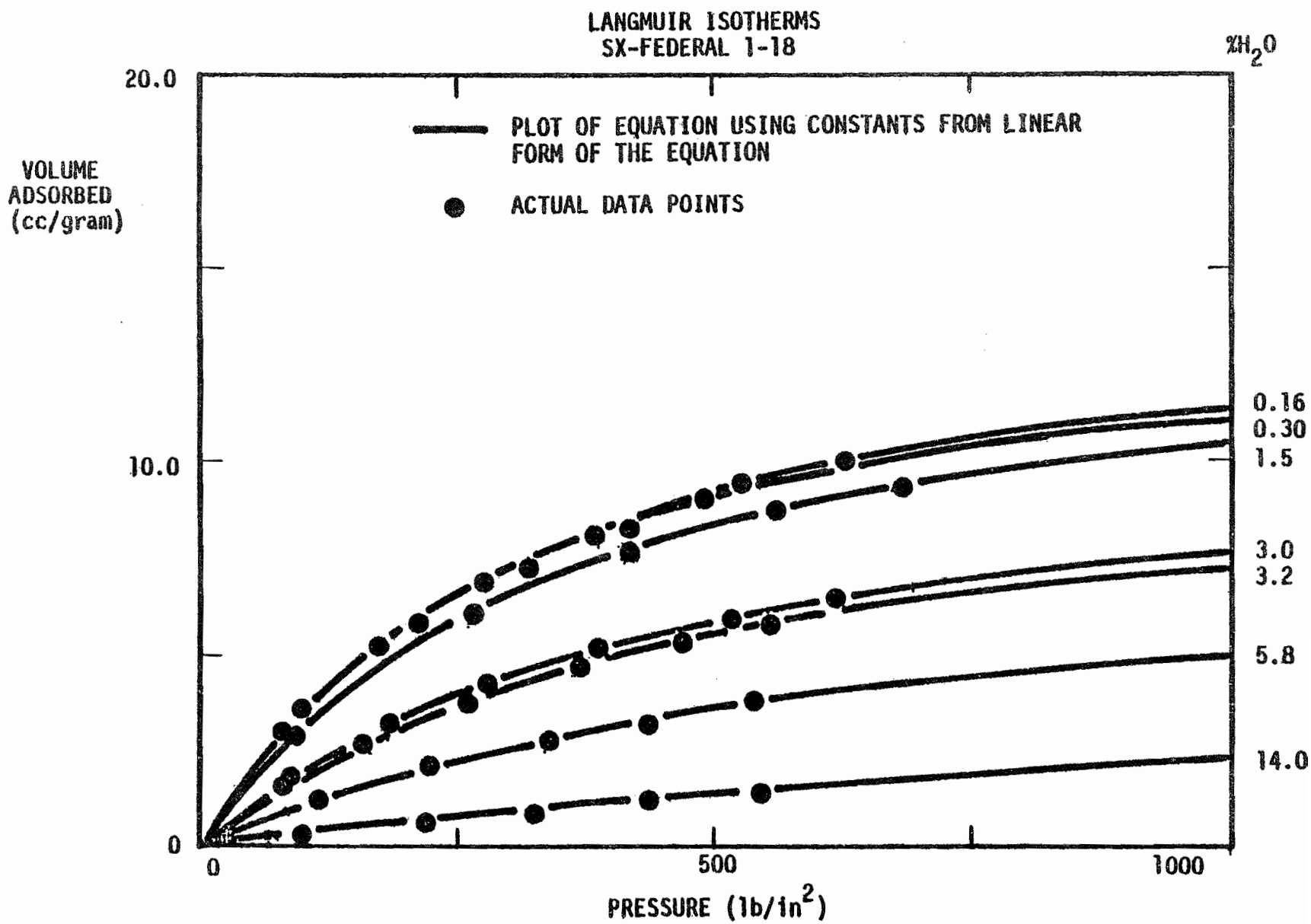

Figure 7 Adsorption of methane on wet coal.

the linearized plots of Figure 8. In that figure it is evident that the slopes of the lines are changing as the water content increases. The typical change in adsorption equilibrium constant with water content is represented in Figure 9 and quantified in Table 5. The systematic decrease in monolayer capacity of the coal for methane is evident. Similar results were obtained for the other coal samples.

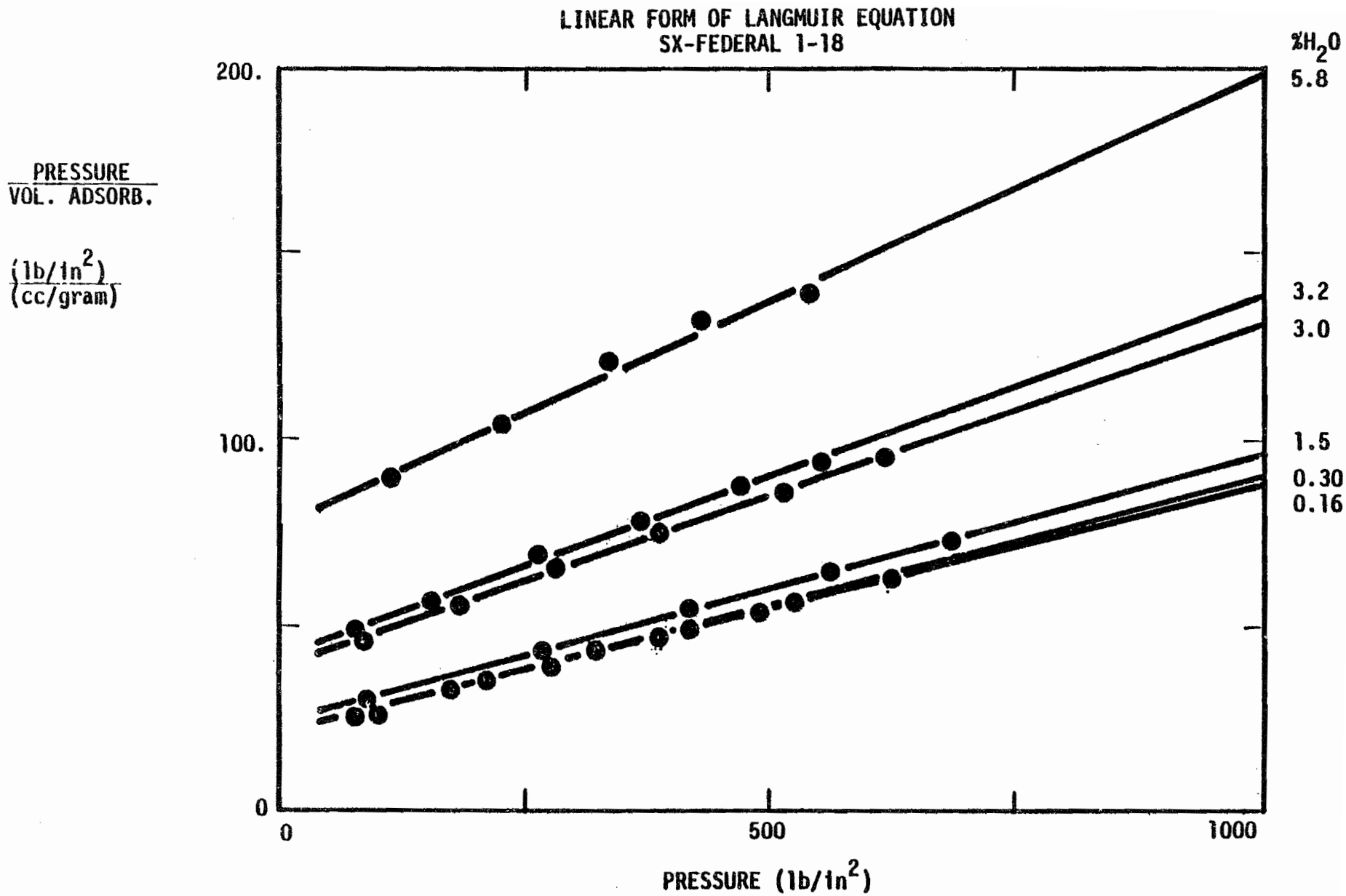

Figure 8 Linearized adsorption isotherms at six water contents.

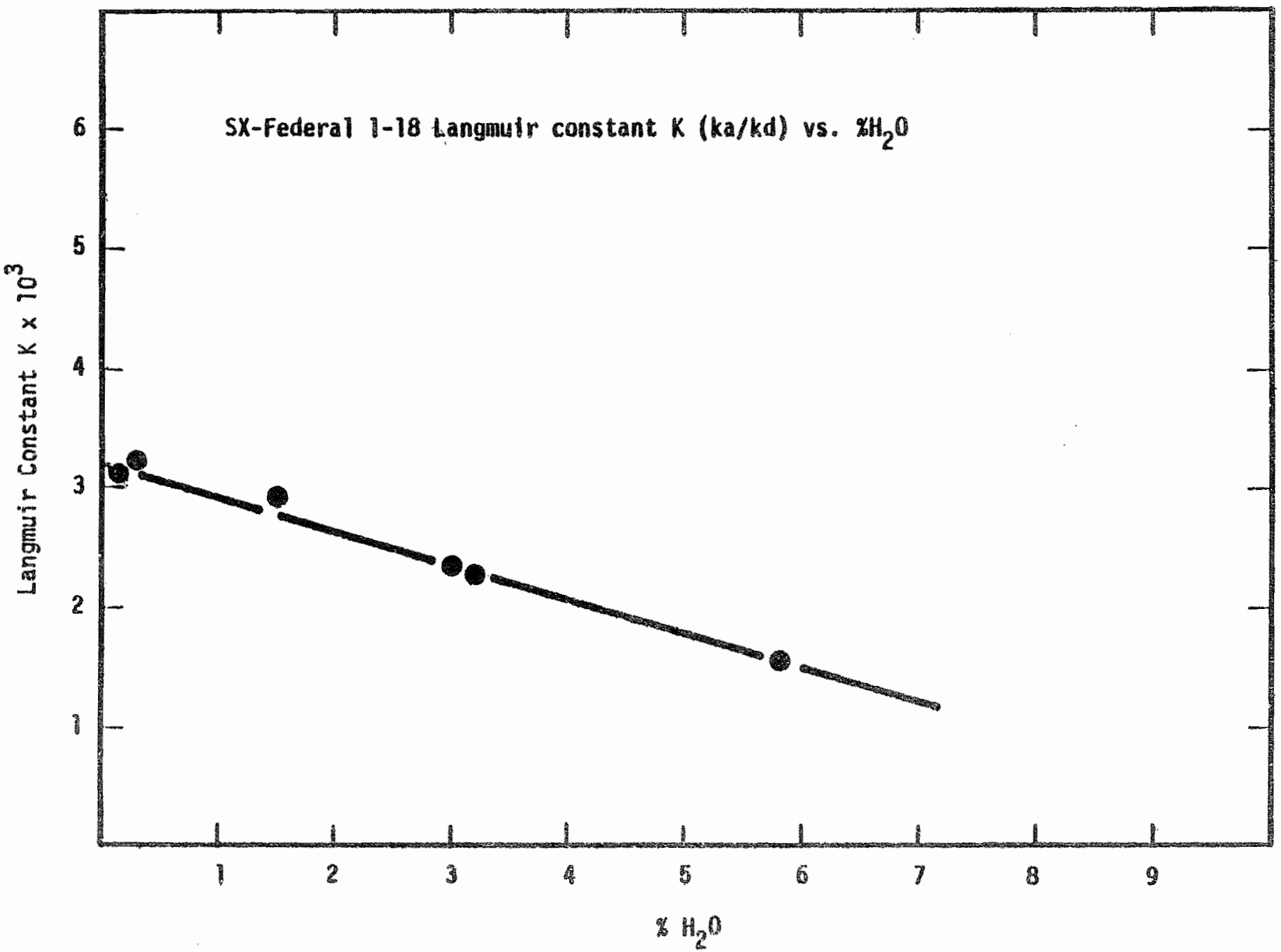

Figure 9 Effect of water content on Langmuir adsorption constant.

Table 5

Variation in Monolayer Capacity and Adsorption Constant as a Function of Water Content

SX-Federal 1-18

Monolayer Capacity (cc/gram)	Langmuir Constant K	$\%H_2O$
14.89	0.003153	0.16
14.62	0.003204	0.30
13.96	0.002940	1.5
10.86	0.002351	3.0
10.41	0.002283	3.2
8.22	0.001582	5.8
7.45	0.000470	14.0

Physical Structure Properties

Characterization of the internal surface and pores of coal has been the objective of this task. In addition to the use of CO_2 and CH_4 for surface area measurements, neopentane was used as a third test adsorbate. These low pressure (< 1 atm) experiments gave consistent results for each gas in that the surface areas determined by CO_2 were higher than those by CH_4 and both CO_2 and CH_4 areas were much higher than those by neopentane. These results reflect the assumed structure of these coals: a bidisperse structure with most of the pores being extremely small (< 20 Å). Complete adsorption isotherms with neopentane do show a pore size distribution consistent with the differences in surface areas for the different adsorbates. The methane capacities found in the high pressure task (previous section) do not agree with those found at low pressures. The difference is ascribed to the fact that these low pressure experiments are only sensitive to high energy binding sites.

Introduction

It is well known that coal is a porous material and it has a high specific surface area. The surface area of coal can be calculated by knowing the monolayer adsorption capacity and molecular size of the adsorbate. Generally, the Brunauer, Emmett, and Teller (BET) equation has been used to calculate the monolayer capacity. Many investigations and studies have also been carried out to determine the validity of the Dubinin-Polanyi equation using carbon dioxide as an adsorbate on carbon, coals and other porous materials. Because most of the gas trapped in coal is adsorbed on the internal surface of coal, it can be presumed that the amount of gas contained in coal depends primarily upon the monolayer adsorption capacity, and the physical properties of the pores, as well as geological influences.

In this task, the relationships which may exist between the gas content data obtained from the chip desorption technique and the adsorption capacity and pore structure of the coals were investigated. This information should help us to understand the basin-wide delineation of the gas content of coalbeds and the mechanism of methane storage in coal beds. The validity of the Dubinin-Polanyi equation with carbon dioxide and methane sorbates was also tested. In addition, general physical properties of Fruitland coal in the San Juan Basin will be described.

Materials

Twelve representative coal samples from the San Juan Basin of New Mexico were selected from among the 33 samples collected from the chip desorption field work. These coal samples are identified by well location and the depth of the coal seams (Table 6). In addition to coal samples, two well-characterized carbon black samples were used for the purpose of standardization and comparison. Methane, carbon dioxide, 2,2-dimethyl propane and nitrogen were used as adsorbates.

Before the monolayer capacity and hysteresis experiments, the ground coal samples were dried at 104 to 110°C for 3 hours in air in a Precision Theco oven. The fluctuation of temperature in the oven is ±2°C. Then, the sample cell was attached to the volumetric adsorption apparatus for overnight outgassing at approximately 10^{-4} torr which was produced by a mechanical vacuum pump.

This work

Monolayer capacities of twelve coal samples using carbon dioxide, methane, and 2,2-dimethyl propane are shown in Table 7. These monolayer capacities were determined from analysis of equilibrium adsorption data with the Dubinin-Polanyi isotherm. The

Table 6

List of Coal Samples
(San Juan Basin, New Mexico)

Sample No.	Identification	Depth (ft)
1	SX-Susco Biddoni #1	1200-1210
2	SX-Federal #1-18	1140-1150
3	Dome #2	1401-1408
4	Dome #3, JL-12	1305-1311
5	B/N 24R, JL-17	3053-3073
6	B/N 24R, JL-18	3096-3105
7	B/N 24R, JL-10	3125-3143
8	B/N 31A, JL-18	2970-2979
9	B/N 45A, JL-9	3006-3015
10	B/N 45A, JL-12	3006-3015
11	N.W. #51	3119-3141
12	Western Coal	surface

Table 7

Monolayer Capacity of San Juan Basin Coal
(unit: cc/g)

Sample No.	Site	CO_2	CH_4	C_5H_{12}
1	Susco-Biddoni #1	14.5	6.7	0.44
2	Federal #1-18	18.25	7.79	0.59
3	Dome #2	15.12	8.34	0.72
4	Dome #3, JL-12	12.88	6.57	0.86
5	24R, JL-17	9.75	5.73	0.58
6	24R, JL-18	9.04	6.09	0.31
7	24R, JL-10	8.35	5.74	0.15
8	31A, JL-18	8.97	5.46	0.47
9	45A, JL-9	10.14	6.78	0.22
10	45A, JL-12	11.87	6.30	0.36
11	N.W. #51	3.83	3.04	0.18
12	Western Coal	15.84	6.88	1.00

plots of the linearized Dubinin-Polanyi equation for carbon dioxide adsorption on twelve coal samples are shown in Figures 10 and 11. The plots for methane adsorption are shown in Figures 12 and 13, and the plots for 2,2-dimethyl propane adsorption are shown in Figures 14 and 15. All plots show a linear relationship of log V versus $[\log(P_0/P)]^2$ with correlation coefficients ranging from -0.999 to -0.99999.

The Dubinin-Polanyi equation using carbon dioxide and methane gives straight lines over the whole range of relative pressures. However, upward curvature has been experienced using 2,2-dimethyl propane at high relative pressure, when the value of $[\log(P_0/P)]^2$ is less than 5. This curvature has been explained by multilayer formation. Among the three adsorbates studied, 2,2-dimethyl propane is the one most likely to condense at room temperature. To avoid this phenomenon, equilibrium points are measured at relative pressures below 0.005.

For all samples, the carbon dioxide capacities are higher than the methane capacities, and the methane capacities are higher than the 2,2-dimethyl propane capacities. Explanations for these differences and descriptions of experiments run to check the results are given in Appendix F.

As a summary of these measurements, we were unable to link the surface properties at low rpessure to either high pressure capacities for methane or in place content.

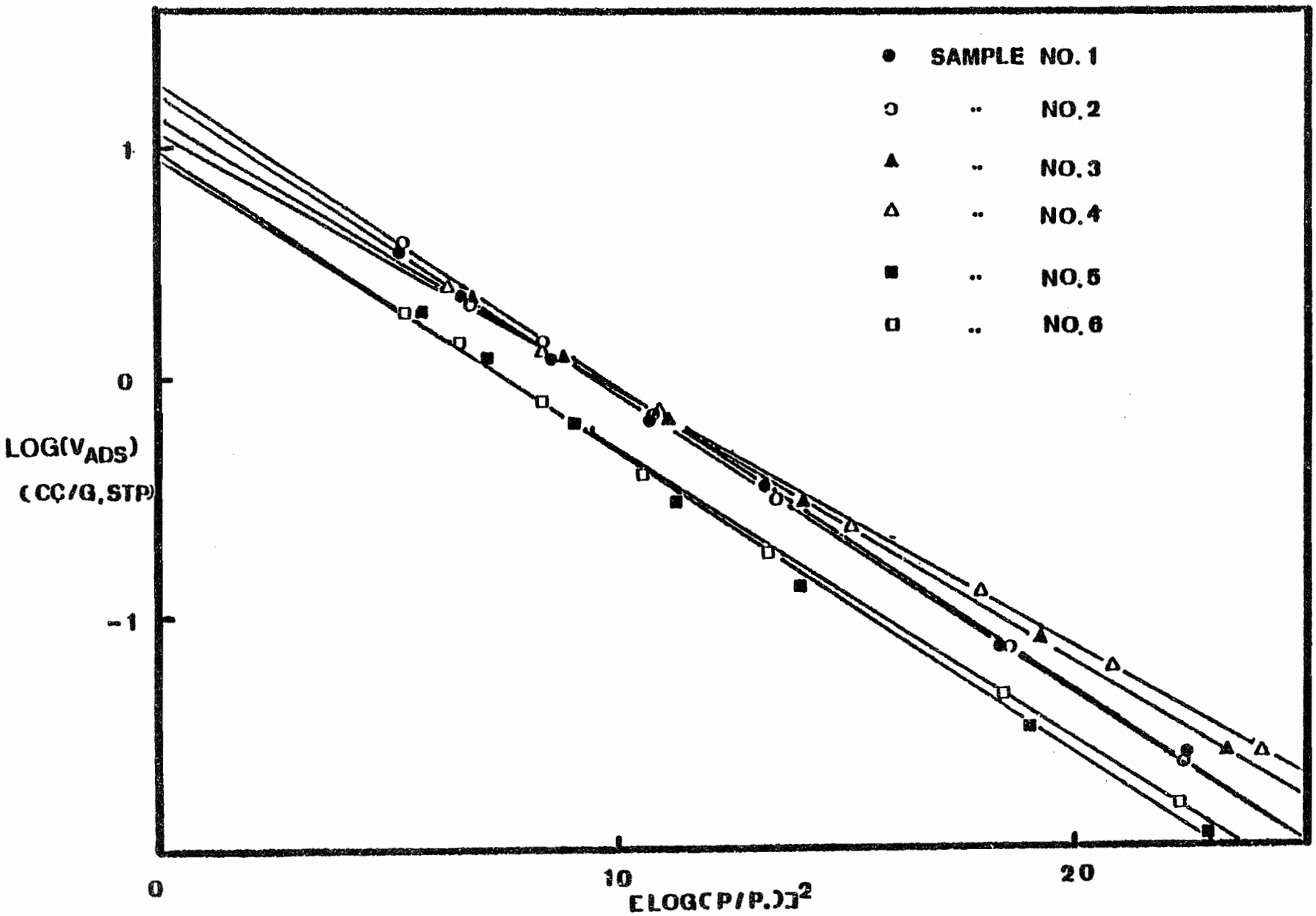

Figure 10. D-P plots of CO_2 adsorption on the coals--I.

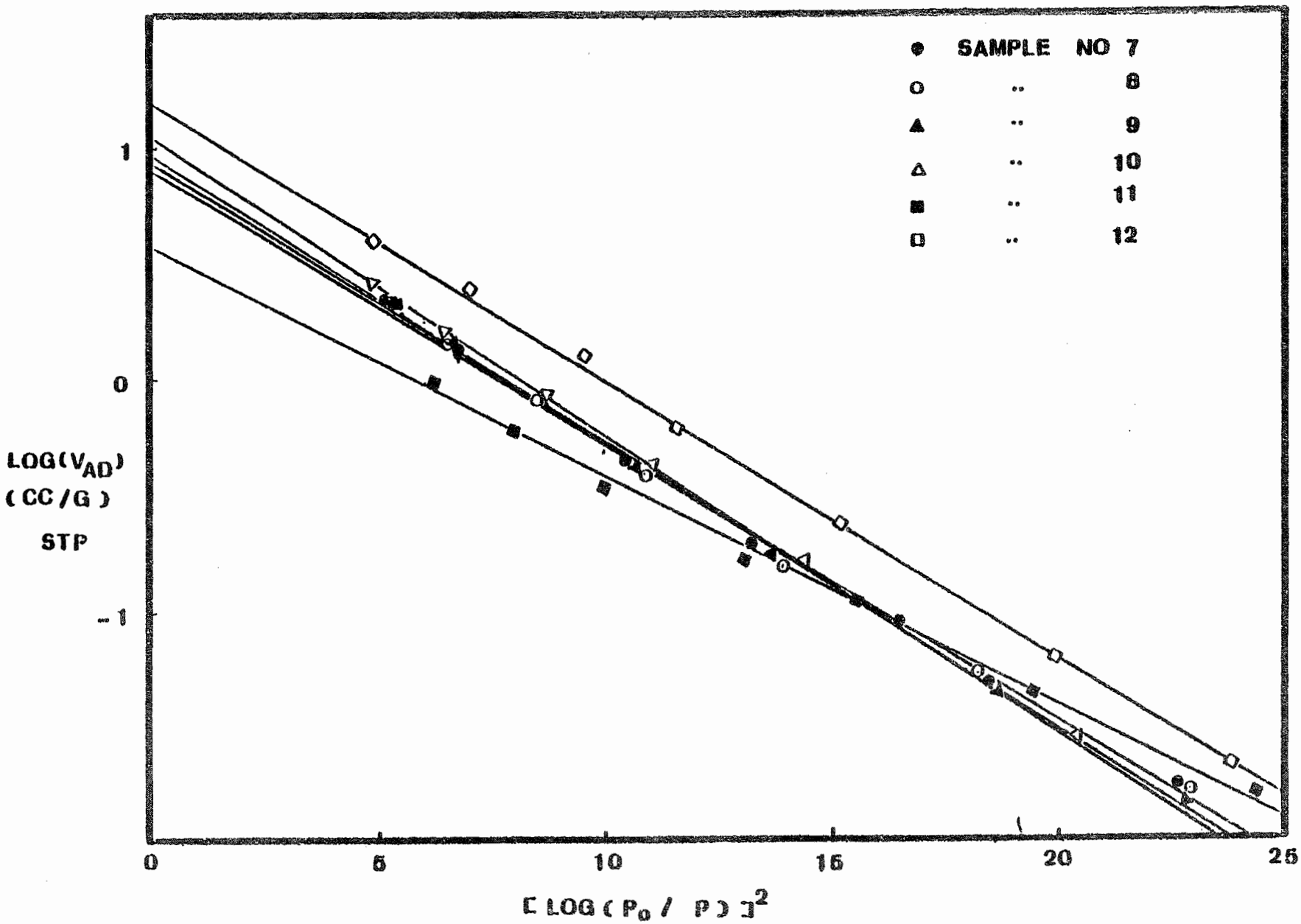

Figure 11 D-P plots of CO_2 adsorption on the coals--II.

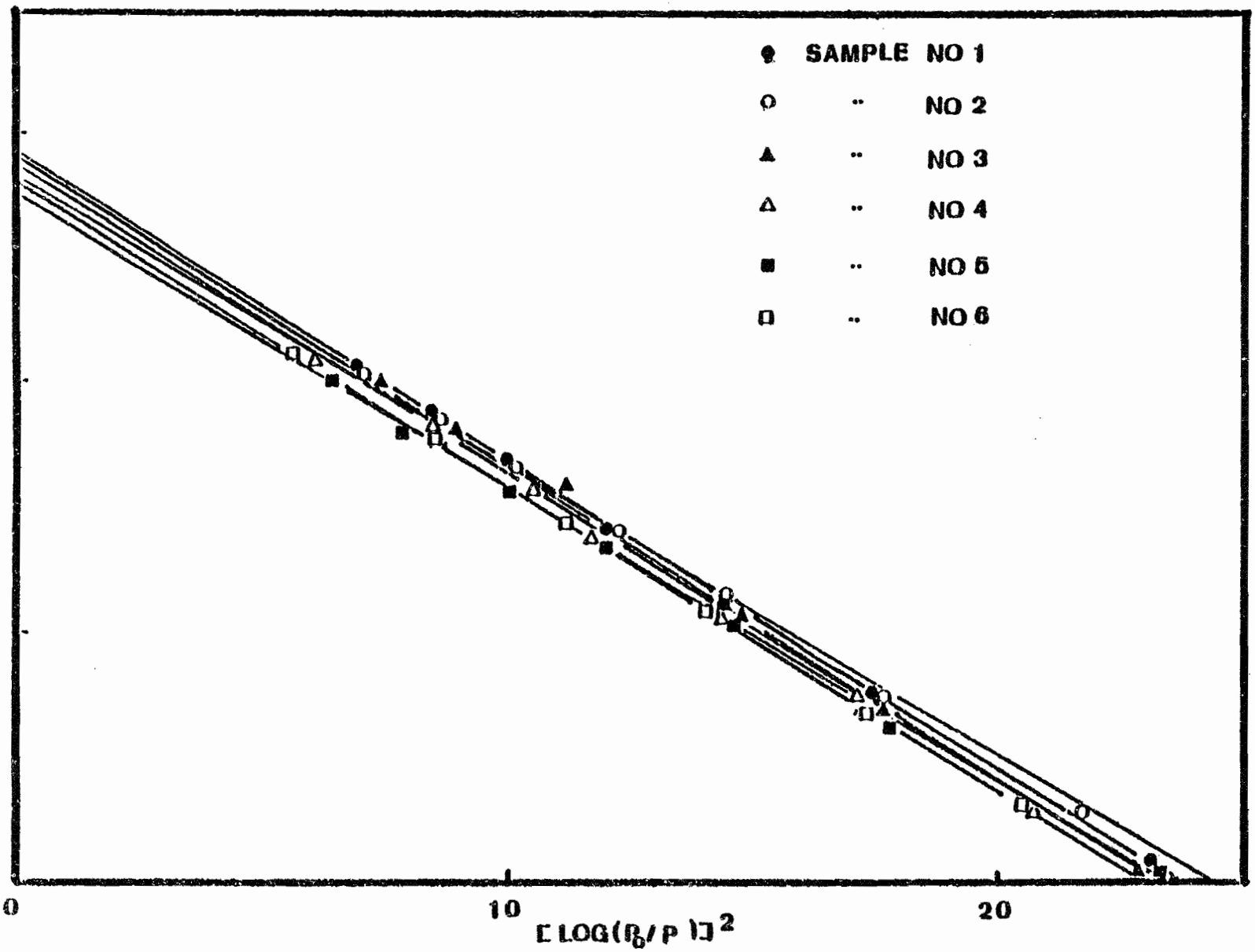

Figure 12 D-P plots of CH_4 adsorption on the coals--I.

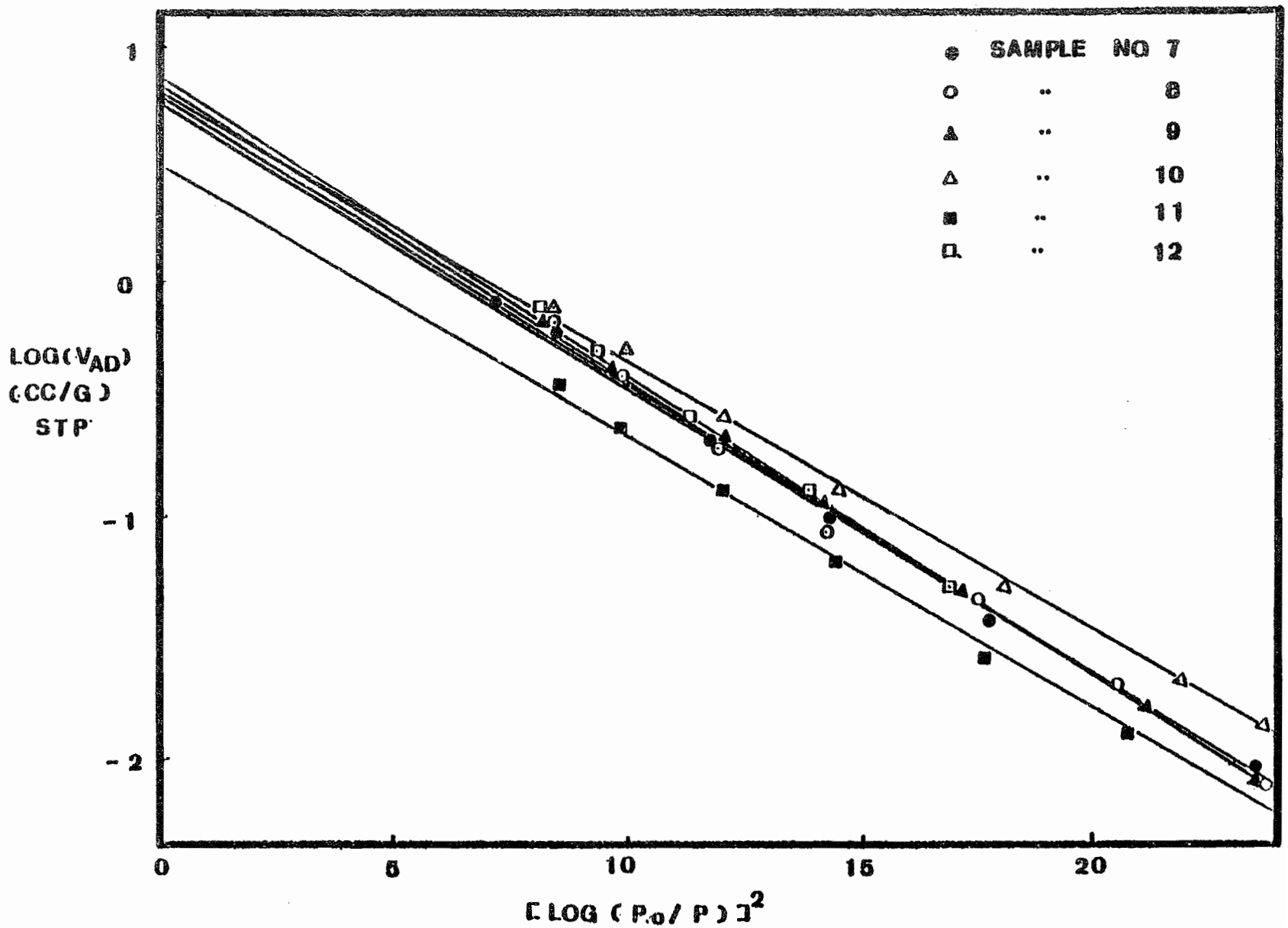

Figure 13 D-P plots of CH_4 adsorption on the coals--II.

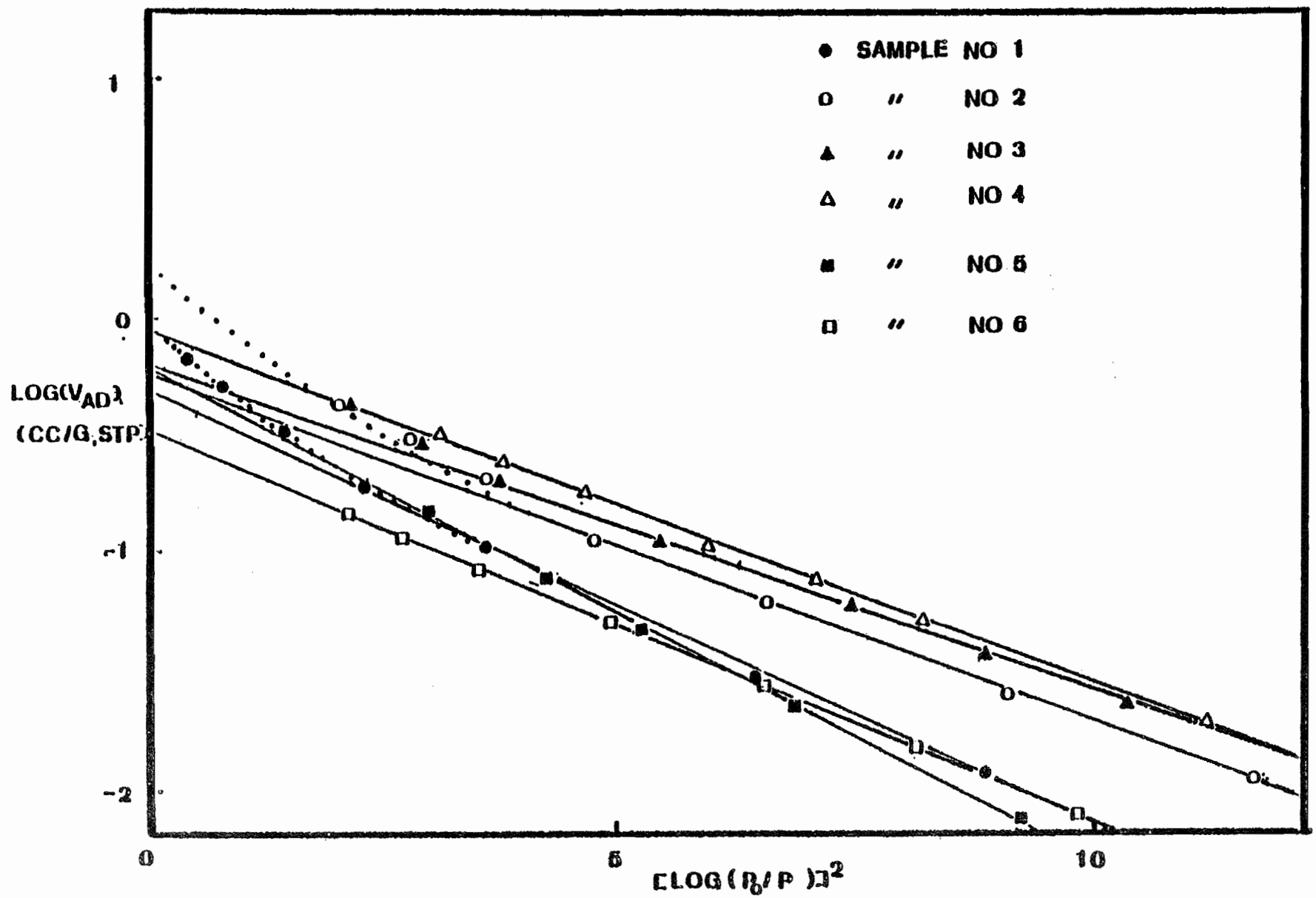

Figure 14 D-P plots of 2,2-dimethyl propane adsorption on the coals--I.

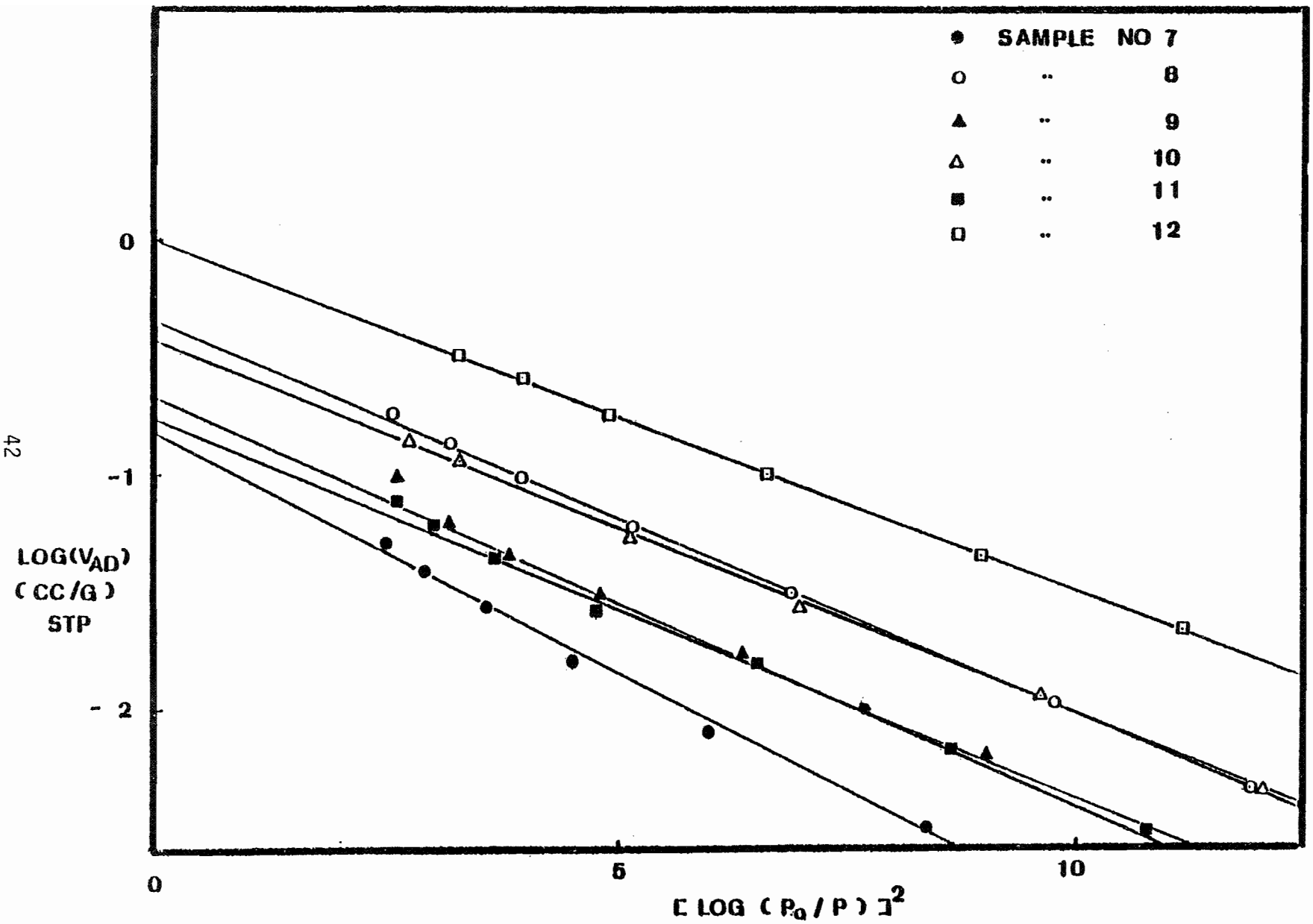

Figure 15 D-P plots of 2,2-dimethyl propane adsorption on the coals--II.

Diffusion of Methane in Coal

The diffusion of methane in coal has been extensively studied with the use of three basic experiments. The evolution of gas from recharged pieces of coal, the stedy-state diffusion of methane through a thin disk of coal, and the dynamic response of diffusion broadened tracer experiments with small pieces of coal have ben used to determine various aspects of the diffusive properties of coal. We have found that methane diffusion through coal is best described by a two-parameter model which can be used as source term in production models. Of the three techniques, the steady-state diffusivities gave results that do not seem to directly apply to production models or correction factors. Those results are not sensitive to the long-term-diffusion characterization parameters. However, they do conveniently show variation for different gases.

Introduction

The desorption and diffusion of methane in coal is of importance both in the determination of the methane content of coal and for use in production models to determine coalbed methane production rates. Since methane is physically adsorbed on coal, it has generally been assumed that the rate of methane released from a single coal particle is controlled by the diffusion of methane through the pore structure of the coal. In modeling methane flows through coal fields, it is normally assumed that the coal consists of blocks interspersed with cracks. The methane is assumed to diffuse through these pores to cracks, in which the mechanism of transport is laminar flow. On the basis of diffusion experiments to be described subsequently, laminar flow in the cracks has been taken to be the rate limiting step and the effects of diffusion and desorption on the overall transport rate

have been treated only empirically. However, the above assumptions are supported with diffusion coefficients which are primarily a measure of macropore diffusion and, hence, are not representative for the entire timescale of desorption.

Despite the practical necessity for the determination of the mechanisms and magnitude of methane diffusion in coal, the problem has received little attention. Studies to date have been of two different types. In one, the rate of desorption from small coal particles after undergoing a step-change in surface concentration is used in conjunction with either a unimodal pore model or empirical description to determine a diffusion coefficient. The second technique is to flow methane or helium through a solid coal disk. With the measured pressure drop and flow rate, a permeability constant (and, hence, diffusion coefficient) may be obtained.

This work

The principal laboratory technique developed for this task was the Pellet String reactor PSR) shown schematically in Figure 16. Pulse injection of methane into the PSR filled with coal pieces results in elution curves like that shown in Figure 17. Results are shown for three types of coal in Table 8.

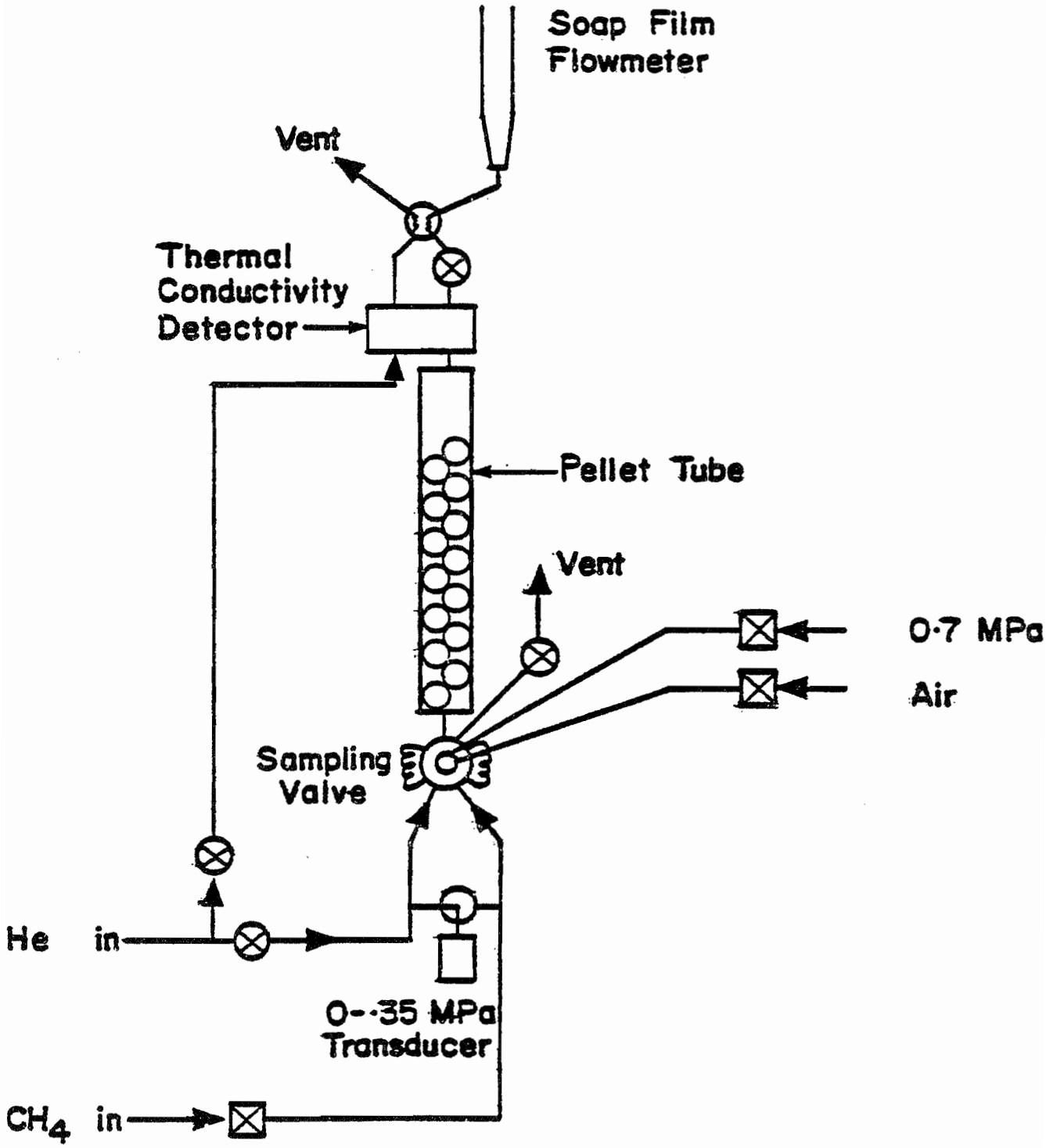

Figure 16 PSR schematic diagram.

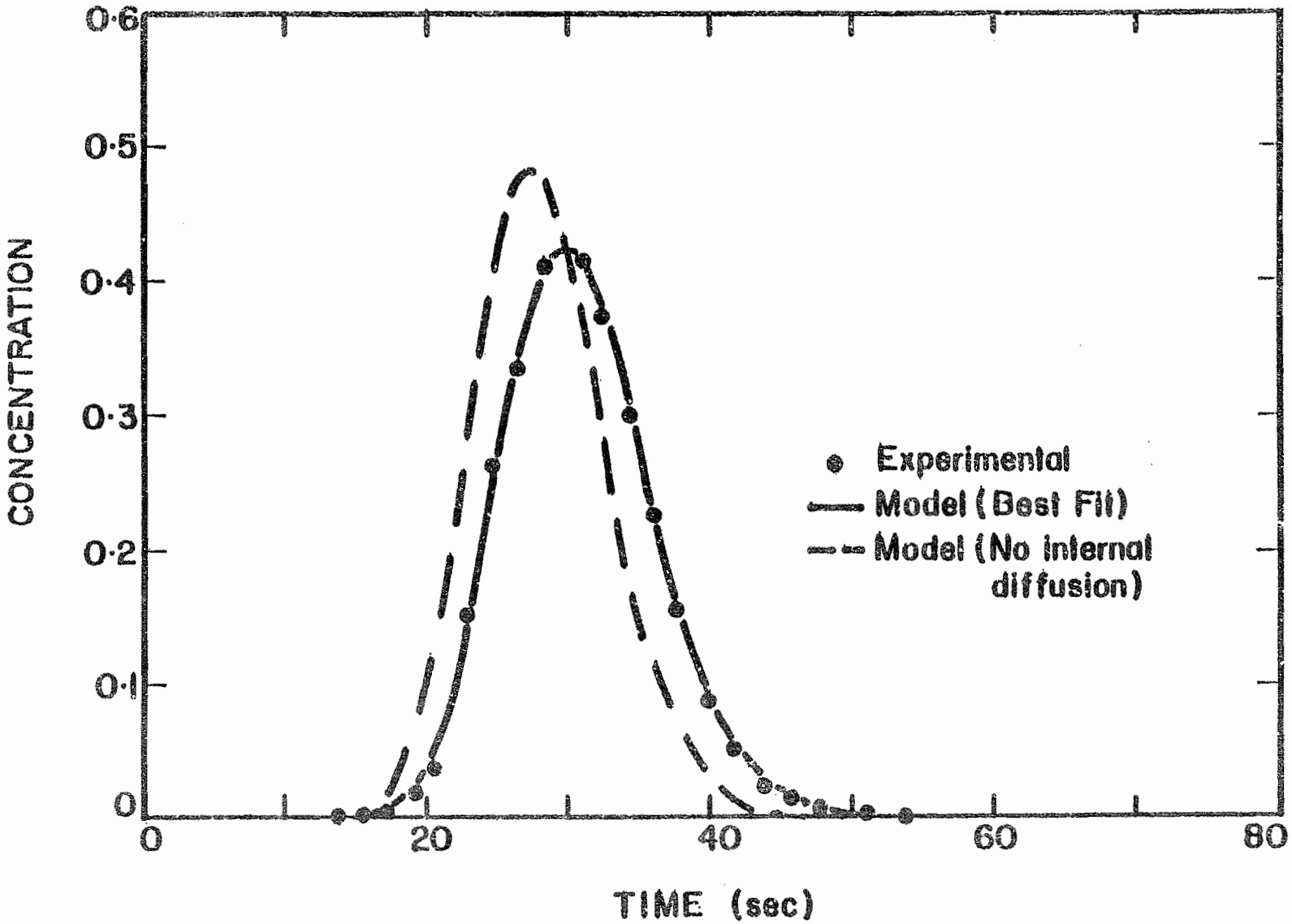

Figure 17 Typical PSR elution curve for methane diffusion in coal.

Table 8

Bidisperse Pore Model Parameters
as Measured with the PSR

Sample	Rank	$D_i \times 10^7$ (sec^{-1})	$D_a \times 10^5$ (sec^{-1})	$\Delta \times 10^7$ (sec^{-1})	$\frac{\Delta}{3D_i}$
Madrid	Anthracite	1.0	1.2	3.7	1.23
Pittsburgh	Bituminous	4.4	5.2	5.9	.45
Fruitland	Subbituminous	11.0	5.6	16.0	.48

These results show trends that are expected for changes in pore structure of the three coals. Full descriptions of the results and the other techniques are given in Appendixes 3, 5, and 8.

From this work we have developed a model for methane evolution into the crack flow regime fo a full production model. The parameters of the model have been measured in three separate types of experiments.

CONCLUSIONS

As a result of our work, we have been able to conclude that:

- the chip desorption technique and associated lost-gas correction factors are valid coalbed methane delineation techniques,
- basin wide coalbed methane delineation is very site specific and seems to defy normal trend expectations. Therefore, multiple site testing is required for reasonable resource definition,
- coalbed methane content appears to be geologically influenced much more strongly than limited by equilibrium adsorption capacity,
- diffusion of methane through coal should be described by a two-parameter model which properly gives gas evolution rates over both short and long times. Such a model has been developed and is directly applicable to production models as a source term.
- surface properties of coal as measured at low ressures do not seem to relate to the high pressure measurements of the methane adsorption capacity.

RECOMMENDATIONS

A number of issues remain unresolved. While the tasks of this project were completed, the need for some further studies become readily apparent.

- The complete validation of the chip desorption technique and the Bureau of Mines' core desorption technique could be accomplished by direct comparison with pressurized core sampling.
- The chip desorption technique needs to be applied to other basins in order to accelerate use of coalbed methane in other regions of the U.S.A.
- The source terms, as modeled in this project, should be put into gas well production models to study the overall effect of bidisperse pore diffusivity on production.
- Strategies need to be developed for locating high concentrations of coalbed methane. From this work it is clear that "deep and thick" is not enough of a clue.
- Because industry is now accepting coalbed methane as a resource, the major unresolved questions are moving toward production enhancement. For example, what drilling fluids, what completion techniques, and what water production are best for a particular basin.

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